Problem 2) a)

$\tilde{A}(V, T, N_A, N_B, N_C, N_D) = -k_BT \ln Q$

$$dA = \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial N_A}\right)_{T,V,N_B,N_C,N_D} dN_A + \left(\frac{\partial A}{\partial N_B}\right) dN_B$$

skipping other subscripts

$$+ \left(\frac{\partial A}{\partial N_C}\right) dN_C + \left(\frac{\partial A}{\partial N_D}\right) dN_D$$

but dV and dT are zero in this process

and $\mu_x = \left(\frac{\partial A}{\partial N_x}\right) \cdot -k_BT$

$$\Rightarrow dA = -k_BT(\mu_A dN_A + \mu_B dN_B + \mu_C dN_C + \mu_D dN_D)$$

as long as not @ $T=0$, can divide by $-k_BT$ on both sides,

using $dN_A = a\, d\lambda$, etc as defined in problem, we get

$$-dA/k_BT = d\lambda\,(a\mu_A + b\mu_B - c\mu_C - d\mu_D)$$

at equilibrium $dA/d\lambda = 0$ means

$$a\mu_A + b\mu_B - c\mu_C - d\mu_D = 0 \quad \checkmark$$

$$Q = \underbrace{\frac{q_A^{N_A}}{N_A!}}_{Q_A} \cdot \underbrace{\frac{q_B^{N_B}}{N_B!}}_{Q_B} \cdot \underbrace{\frac{q_C^{N_C}}{N_C!}}_{Q_C} \cdot \underbrace{\frac{q_D^{N_D}}{N_D!}}_{Q_D}$$

$$\mu_A = -k_BT\frac{\partial \log Q_A}{\partial N_A} - k_BT \cancel{\frac{\partial \log(Q_B Q_C Q_D)}{\partial N_A}} \to 0$$

$$= -k_BT\frac{\partial}{\partial N_A}\Big(N_A\log q_A - \underbrace{\log N_A!}_{\approx (N_A\log N_A - N_A)}\Big)$$

$$\approx -k_BT\cdot\Big(\log q_A - \big(N_A\cdot\tfrac{1}{N_A} + \log N_A - 1\big)\Big)$$

$$= -k_BT\log(q_A/N_A)$$

Plugging in to Eqn 4 gives

$$0 = -k_B T \left(a \log q_A/N_A + b \log q_B/N_B - c \log q_C/N_C - d \log q_D/N_D \right)$$

$$\Rightarrow \quad 0 = \log\left[\left(q_A/N_A\right)^a \left(q_B/N_B\right)^b \cdot \left(q_C/N_C\right)^{-c} \cdot \left(\frac{q_D}{N_D}\right)^{-d} \right]$$

exponentiate both sides

$$\Rightarrow \quad 1 = \left[\left(q_A/N_A\right)^a \left(q_B/N_B\right)^b \cdot \left(q_C/N_C\right)^{-c} \cdot \left(\frac{q_D}{N_D}\right)^{-d} \right]$$

note that $q_A/N_A = (q_A/V)/(N_A/V) = \dfrac{(q_A/V)}{\rho_A}$

$$\Rightarrow \left((q_C/V)/\rho_C\right)^c \cdot \left((q_D/V)/\rho_D\right)^d = \left(\frac{(q_A/V)}{\rho_A}\right)^a \left(\frac{(q_B/V)}{\rho_B}\right)^b$$

$$\Rightarrow \quad \frac{\rho_D^d \rho_C^c}{\rho_A^a \rho_B^b} = \frac{(q_D/V)^d (q_C/V)^c}{(q_A/V)^a (q_B/V)^b} \equiv K(T) \quad \checkmark$$

The right side depends only on T because each $q_X = V f(n_X, T)$ as in the problem, so all V dependence cancels out, and no N's. Other side $\rho_X = P_X/k_B T$ where P_X is the partial pressure, see next parts

$$A = -k_B T \log Q$$

$$Q = Q_A Q_B Q_C Q_D \quad \text{as above}$$

$$A = -k_B T \left[\log Q_A + \log Q_B + \log Q_C + \log Q_D\right]$$

$$A_x = -k_B T \log Q_x = -k_B T \log\left(\frac{q_x^{N_x}}{N_x!}\right) \checkmark$$

d) $$P_x = -\frac{\partial A_x}{\partial V} = +k_B T \frac{\partial}{\partial V}\left(\log \frac{q_x^{N_x}}{N_x!}\right)$$

$$= k_B T \frac{\partial}{\partial V}\left(N_x \log V + N_x \log f - \log N!\right)$$

$$= N_x k_B T / V = \rho_x k_B T$$

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{\rho_C^c \rho_D^d}{\rho_A^a \rho_B^b} \cdot (k_B T)^{cd-ab}$$

$$= K(T) \cdot (k_B T)^{cd-ab}$$